

**MASTER COPY:** PLEASE KEEP THIS "MEMORANDUM OF TRANSMITTAL" BLANK FOR REPRODUCTION PURPOSES. WHEN REPORTS ARE GENERATED UNDER THE ARO SPONSORSHIP, FORWARD A COMPLETED COPY OF THIS FORM WITH EACH REPORT SHIPMENT TO THE ARO. THIS WILL ASSURE PROPER IDENTIFICATION. NOT TO BE USED FOR INTERIM PROGRESS REPORTS; SEE PAGE 2 FOR INTERIM PROGRESS REPORT INSTRUCTIONS.

**MEMORANDUM OF TRANSMITTAL**

U.S. Army Research Office  
ATTN: AMSRL-RO-BI (TR)  
P.O. Box 12211  
Research Triangle Park, NC 27709-2211

- Reprint (Orig + 2 copies)       Technical Report (Orig + 2 copies)  
 Manuscript (1 copy)      X Final Progress Report (Orig + 2 copies)  
     Related Materials, Abstracts, Theses (1 copy)

CONTRACT/GRANT NUMBER: **DAAD19-99-1-0317**

REPORT TITLE:

**Spectroscopy and Device Performance of Rare Earth doped III-V nitrides**

is forwarded for your information.

SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

Uwe Hommerich

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE November 12, 2002		3. REPORT TYPE AND DATES COVERED Final; 7/1/1999-12/31/2002	
4. TITLE AND SUBTITLE  Spectroscopy and Device Performance of Rare Earth doped III-V Nitrides				5. FUNDING NUMBERS  DAAD19-99-1-0317	
6. AUTHOR(S) Uwe Hommerich					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Hampton University, Department of Physics, Hampton, VA 23666				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER  Proposal No. P-40103-EL	
11. SUPPLEMENTARY NOTES  The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
12 a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  The recent demonstration of visible thin-film electroluminescence (TFEL) devices based on rare earth doped GaN has spurred great interest in this class of materials for possible applications in full color displays. Prime candidates for red-green-blue (RGB) emission are the rare earth ions Eu <sup>3+</sup> (red), Er <sup>3+</sup> (green), and Tm <sup>3+</sup> (blue). A full-color TFEL phosphor system based on RE doped GaN has been demonstrated with high brightness (500-1000 cd/m <sup>2</sup> ) under direct current operation of GaN: Er films on Si and sapphire substrates. The recent results on RE doped GaN have shown that these materials are promising for electroluminescent devices operating at room temperature. However, the initial results also indicated that more fundamental studies on the incorporation and excitation mechanisms of RE ions in III-nitrides are necessary to optimize their device performance.					
In this final report, spectroscopic results focusing on the infrared and visible emission from Er <sup>3+</sup> in GaN are presented. The results include a comparison of the optical properties of in-situ Er doped GaN prepared by metalorganic MBE and solid-source MBE. In addition, detailed spectroscopic studies on Er doped GaN prepared by SSMBE as a function of excitation wavelengths, temperature, and pump power are discussed. Finally, initial result on the optical properties of Eu doped GaN are summarized.				14. SUBJECT TERMS  Gallium Nitride, Rare Earth doping; Photoluminescence; Light emitting diodes	
15. NUMBER OF PAGES				16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT <b>UNCLASSIFIED</b>		18. SECURITY CLASSIFICATION ON THIS PAGE <b>UNCLASSIFIED</b>		19. SECURITY CLASSIFICATION OF ABSTRACT <b>UNCLASSIFIED</b>	
20. LIMITATION OF ABSTRACT <b>UL</b>					

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)

Prescribed by ANSI Std. Z39-18  
298-102

**SPECTROSCOPY AND DEVICE PERFORMANCE  
OF RARE EARTH DOPED III-NITRIDES**

**FINAL PROGRESS REPORT**

**Uwe Hömmerich**

**November 12, 2002**

**U.S. ARMY RESEARCH OFFICE**

**GRANT DAAD19-99-1-0317**

**HAMPTON UNIVERSITY**

---

## **TABLE OF CONTENTS**

TABLE OF CONTENTS	4
BODY OF REPORT	
A. STATEMENT OF PROBLEM	5
B. SUMMARY OF MOST IMPORTANT RESEARCH RESULTS	6
<i>Comparison of the optical properties of Er<sup>3+</sup> doped GaN         Prepared by metal-organic MBE and solid-source MBE</i>	6
<i>Spectroscopic studies of Er doped GaN (SSMBE) as a         function of excitation wavelength, temperature, and         pump power</i>	8
<i>Initial spectroscopic studies of Eu doped GaN (SSMBE)</i>	12
C. LIST OF PUBLICATIONS AND TECHNICAL REPORTS	16
D. SCIENTIFIC PERSONNEL	19
INVENTIONS	19
BIBLIOGRAPHY	20

## BODY OF REPORT

### **A. STATEMENT OF THE PROBLEM STUDIED**

III-nitride semiconductors have received world-wide attention because of applications as blue LED's, lasers, UV detectors, and high temperature electronic devices. The large bandgap of III-nitrides (InN: 1.9 eV, GaN: 3.4 eV, and AlN: 6.2 eV) makes these materials also interesting hosts for rare earth (RE) doping for potential applications in optoelectronics [1-4]. Most previous work on RE doping of semiconductors has focused on the 1.54  $\mu\text{m}$  emission from Er<sup>3+</sup> ions because of applications in optical communications [1,2]. As demonstrated by several research groups, Er doped into wide-gap semiconductors exhibited a reduced emission quenching compared to Er doped into narrow-gap materials like Si and GaAs [1,2]. Stable 1.54  $\mu\text{m}$  emission up to temperatures as high as 550 K has been observed from Er implanted GaN thin films [5]. In 1996, the first observation of 1.54  $\mu\text{m}$  electroluminescence using Er implanted GaN was reported [6]. The recent demonstration of visible thin-film electroluminescence (TFEL) devices based on rare earth doped GaN has spurred great interest in this class of materials for possible applications in full color displays [3,4]. Prime candidates for red-green-blue (RGB) emission are the rare earth ions Eu<sup>3+</sup> (red), Er<sup>3+</sup> (green), and Tm<sup>3+</sup> (blue). A full-color TFEL phosphor system based on RE doped GaN has been demonstrated with high brightness (500-1000 cd/m<sup>2</sup>) under direct current operation of GaN: Er films on Si and sapphire substrates [3,4]. The recent results on RE doped GaN have indicated that these materials are promising for electroluminescent devices operating at room temperature. However, the initial reports also indicated that more fundamental studies on the incorporation and excitation mechanisms of RE ions in III-nitrides are necessary to optimize their device performance.

In this final report, spectroscopic results focusing on the infrared and visible emission from Er<sup>3+</sup> in GaN are presented. The results include a comparison of the optical properties of in-situ Er doped GaN prepared by metalorganic MBE and solid-source MBE. In addition, detailed spectroscopic studies on Er doped GaN prepared by SSMBE as a function of excitation wavelengths, temperature, and pump power are discussed. Finally, initial result on the optical properties of Eu doped GaN are summarized.

## B. SUMMARY OF MOST IMPORTANT RESEARCH RESULTS

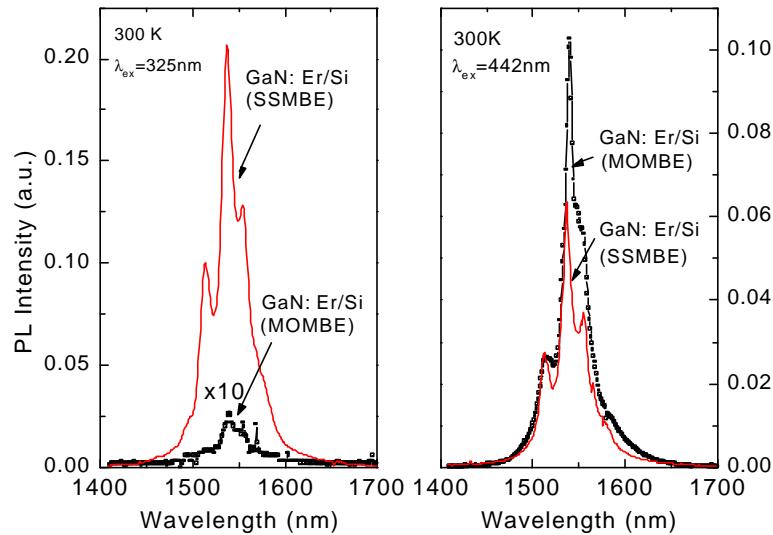
The research results of this project have been discussed in great detail in 8 refereed journal publications and 1 book chapter. Available reprints are attached to this final report as pdf-files.

In the following the most important research results are briefly summarized:

### 1. Comparision of the optical properties of Er<sup>3+</sup> doped GaN prepared by metalorganic MBE and solid-source MBE

We investigated the visible and infrared luminescence properties of Er doped GaN grown prepared by metalorganic molecular beam epitaxy (MOMBE) and solid-source molecular beam epitaxy (SSMBE) on Si substrates. The Er doped GaN sample prepared by MOMBE was grown at the University of Florida (Dr. Abernathy's group) in an INTEVAC Gas Source Gen II on In-mounted (100) Si substrate [7]. The GaN film was preceded by a low temperature AlN buffer layer ( $T_g=425$  °C). An undoped GaN spacer 0.2 μm thick was deposited prior to the growth of GaN: Er. Triethylgallium (TEGa) and Dimethylethylamine alane (DMEAA) provided the group III fluxes. A shuttered effusion oven with 4N Er was used for solid source doping. Reactive nitrogen species were provided by a SVT radio frequency (rf) plasma source. The Er concentration in the sample was  $\sim 8 \times 10^{18} \text{ cm}^{-3}$ . Due to the incorporation of carbon and oxygen from residual ether in TEGa, the C and O background were  $\sim 10^{21} \text{ cm}^{-3}$  and  $\sim 10^{20} \text{ cm}^{-3}$ , respectively, as measured by SIMS. The Er doped GaN samples prepared by SSMBE was grown at the University of Cincinnati (Dr. Steckl's group) in a Riber MBE-32 system on Si (111) substrates [8]. Ga and Er solid sources were used in conjunction with a RF plasma source supplying atomic nitrogen. The sample was pretreated by cleaning in acetone, methanol, and de-ionized water before insertion into the loadlock. The sample was subsequently outgassed at  $\sim 950^\circ\text{C}$  before growth. During the growth, the Ga cell temperature was kept constant for a beam equivalent pressure of  $\sim 8.2 \times 10^{-7}$  torr. The RF plasma source was kept constant at 400 W with a N<sub>2</sub> flow rate of 1.5 sccm, corresponding to a chamber pressure of mid  $-10^5$  Torr. The growth temperature was varied from 750-950°C and the Er cell temperature was maintained at 1100°C. The Er concentration in the sample was determined by SIMS to be  $\sim 2 \times 10^{20} \text{ cm}^{-3}$ .

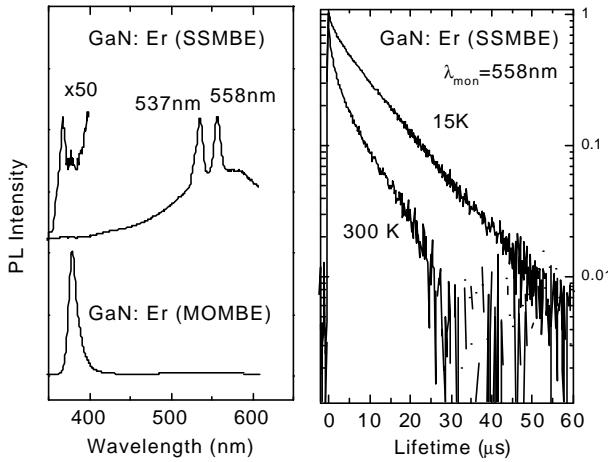
Both types of Er doped GaN samples emitted characteristic 1.54 μm PL resulting from the intra-4f Er<sup>3+</sup> transition  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  as shown in Figure 1. Under below-gap excitation the samples exhibited very similar 1.54 μm PL intensities. On the contrary, under above-gap excitation GaN: Er (SSMBE) showed ~80 times more intense 1.54 μm PL than GaN: Er (MOMBE).



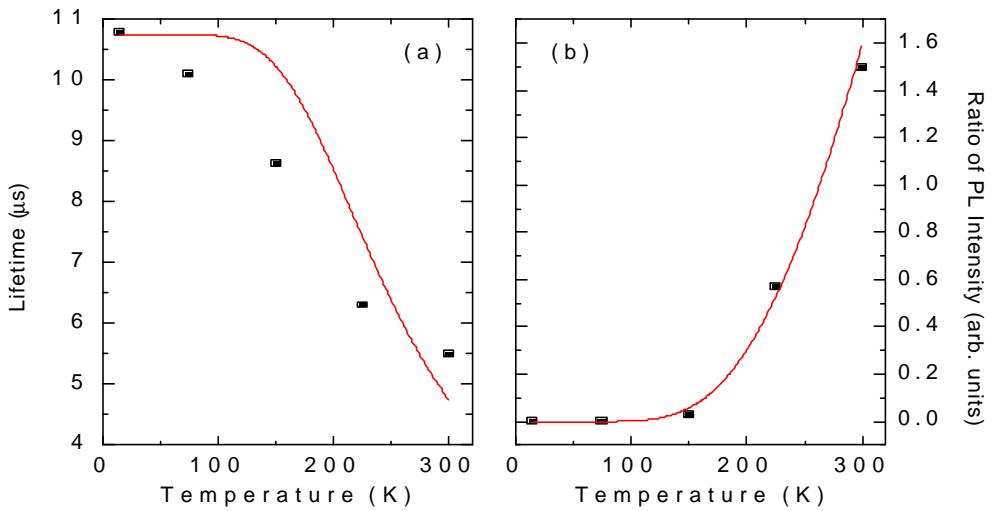
**Figure 1:** 1.54 μm PL spectra of GaN: Er (MOMBE) and GaN: Er (SSMBE) at room temperature. The PL was excited with either the 325 nm (above-gap) or 442 nm (below-gap) line of a HeCd laser.

The weak 1.54  $\mu\text{m}$  PL observed under above-gap excitation from GaN: Er (MOMBE) can be explained by a significantly reduced excitation efficiency compared to below-gap excitation. Visible PL studies (see below) revealed, that for GaN: Er (MOMBE) the bandedge provides an efficient radiative recombination channel reducing the excitation efficiency of intra-4f Er transitions. The excitation wavelength dependent PL study suggests that only weak electroluminescence can be expected from forward-biased GaN: Er (MOMBE) LED's.

Besides strong 1.54  $\mu\text{m}$  PL, GaN: Er (SSMBE) also emitted intense green luminescence at 537 nm and 558 nm, which was not observed from GaN: Er (MOMBE) as shown in figure 2. The GaN: Er (SSMBE) exhibited a weak bandedge PL at  $\sim$ 369 nm (3.36 eV) and two “green” lines located at 537 nm and 558 nm. The green luminescence can be assigned to the intra 4f  $\text{Er}^{3+}$  transitions  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ . The GaN: Er (MOMBE) sample showed strong bandedge PL located at  $\sim$ 381 nm (3.25 eV), however, no indication of green  $\text{Er}^{3+}$  luminescence was found. As discussed before, for GaN: Er (MOMBE) the bandedge provides an efficient radiative recombination channel, which reduces the excitation efficiency for both infrared and visible  $\text{Er}^{3+}$  transitions. Figure 2b) shows the decay transients of the green  $\text{Er}^{3+}$  PL at different temperatures. The lifetime was found to be non-exponential at all temperatures and decreased with increasing temperature. The average lifetimes for the 558 nm line at 15 K and room temperature were determined to be 10.8  $\mu\text{s}$  and 5.5  $\mu\text{s}$ , respectively.



**Figure 2:** a) Visible PL spectra from GaN: Er (SSMBE) and GaN: Er (MOMBE) at 300 K ( $\lambda_{\text{ex}}=325\text{ nm}$ ).  
b) Decay transients of the visible PL at 558 nm from GaN: Er (SSMBE) at 15 K and 300 K ( $\lambda_{\text{ex}}=495\text{ nm}$ ).



**Figure 3:** a) Green PL lifetime of GaN: Er (SSMBE). The solid line describes the change in lifetime according to equation (1). b) Ratio of the PL intensities of the green lines as a function of temperature.

A more detailed study on the temperature dependence of the lifetime was carried out and is depicted in Figure 3a). The thermalization of the  $^4S_{3/2}$  and  $^2H_{11/2}$  states leads to a common decay time  $\tau$  (effective spontaneous emission probability), which can be described as:

$$\frac{1}{t} = \frac{t_s^{-1} + t_h^{-1} \cdot \frac{g_h}{g_s} \exp\left(\frac{-\Delta E}{kT}\right)}{1 + \frac{g_h}{g_s} \exp\left(\frac{-\Delta E}{kT}\right)} \quad (1)$$

where  $\tau_h$  and  $\tau_s$  are the intrinsic radiative decay times of the  $^2H_{11/2} \rightarrow ^4I_{15/2}$  and  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transitions, respectively.  $g_h$  and  $g_s$  are the electronic degeneracies ( $2J+1$ ) of the  $^2H_{11/2}$  and  $^4S_{3/2}$  states and  $\Delta E$  is their energy difference ( $\Delta E=87\text{meV}$ ).

At low temperatures the  $^2H_{11/2}$  state is not thermally populated and the experimental lifetime can be approximated as the intrinsic decay time of the  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transition, i.e.  $\tau_s=10.8\text{\AA}$ s. It is assumed in this approximation that the low temperature decay time is purely radiative. The intrinsic lifetime of the  $^2H_{11/2} \rightarrow ^4I_{15/2}$  is not experimentally accessible, unless a careful analysis of absorption data is carried out, which is rather difficult for thin film materials. It is possible, however, to obtain a rough estimation of the intrinsic decay time  $\tau_h$  from the temperature dependence of the luminescence intensity of the green Er<sup>3+</sup> lines at 537 nm and 558 nm. The intensity of the  $^4S_{3/2}$  line decreased with increasing temperature, whereas the  $^2H_{11/2}$  line had a maximum of intensity at around 300 K. The ratio of the 537 nm and 558 nm lines was calculated and is plotted in Fig 3b). Considering the thermal coupling of the involved states, the intensity ratio of both lines was fitted to an expression

$$I_h = \frac{t_s \cdot g_h \cdot h\nu_h}{t_h \cdot g_s \cdot h\nu_s} \cdot \exp(-\Delta E/kT) \quad (2)$$

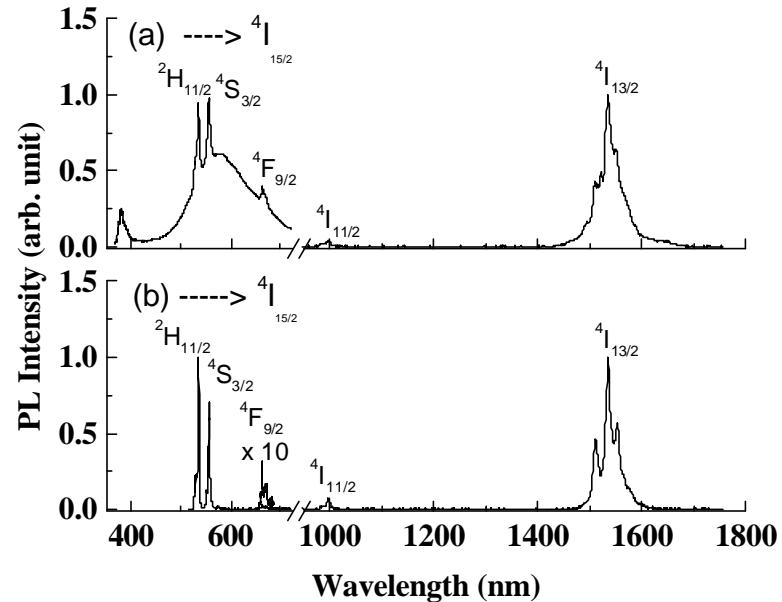
with  $\hbar\nu_h=2.309\text{eV}$ ,  $\hbar\nu_s=2.222\text{eV}$ ,  $\tau_s=10.8\text{\AA}$ s and  $\Delta E=87\text{ meV}$ .  $\tau_h$  was taken as a fitting parameter and the best fit to the data yielded  $\tau_h=0.75\text{\AA}$ s. The fitting result shows that the radiative rate of the  $^2H_{11/2} \rightarrow ^4I_{15/2}$  transition is much larger than that of the  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transition, consistent with published data on Er doped insulators [9]. Using this set of parameters the temperature dependence of the luminescence lifetime was calculated according to equation (1) and is shown in Fig. 3a). The modeling reveals that the decrease of the luminescence lifetime with temperature is mainly due to an increased radiative decay rate arising from the fast thermalization of the  $^2H_{11/2} \rightarrow ^4I_{15/2}$  and  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transitions. This analysis of the lifetime implies that non-radiative decay processes are small and therefore the green luminescence efficiency is near unity.

## **2. Spectroscopic studies of Er<sup>3+</sup> doped GaN (SSMBE) as a function of excitation wavelength, temperature, and pump power**

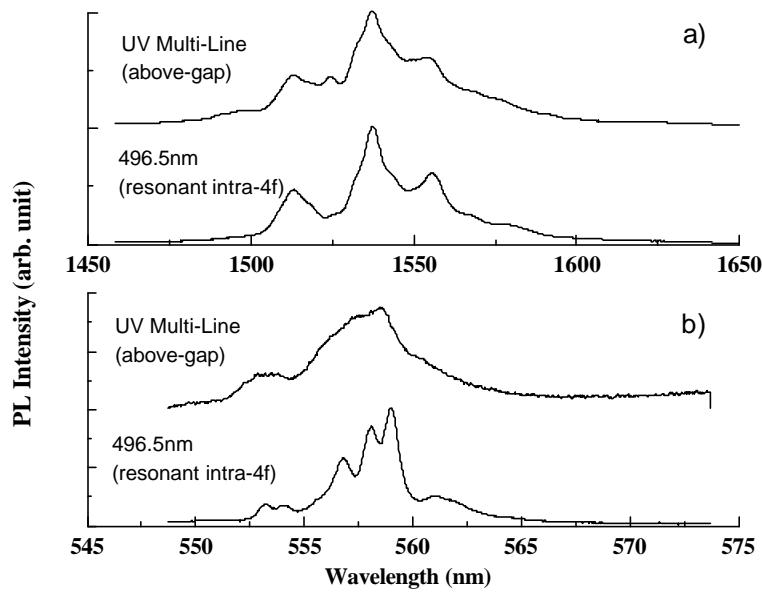
### **Wavelength dependent PL measurements:**

The visible and infrared luminescence of Er doped GaN prepared by SSMBE were investigated in more detail as a function of excitation wavelength, temperature, and pump power. The PL spectra of GaN: Er (SSMBE), measured at room temperature, using above-gap (336-363 nm) and below-gap (496.5 nm) excitation are shown in Fig. 4. With above-gap pumping three PL features can clearly be distinguished (see Fig. 1a): the band-edge signal from GaN located at ~369 nm, a defect-related yellow-band PL centered at ~550 nm, and several intra-4f Er<sup>3+</sup> transitions. The intra-4f Er<sup>3+</sup> transitions are identified as: 537 nm ( $^2H_{11/2} \rightarrow ^4I_{15/2}$ ), 558 nm ( $^4S_{3/2} \rightarrow ^4I_{15/2}$ ), 667 nm ( $^4F_{9/2} \rightarrow ^4I_{15/2}$ ), 1000 nm ( $^4I_{11/2} \rightarrow ^4I_{15/2}$ ), and 1540 nm ( $^4I_{13/2} \rightarrow ^4I_{15/2}$ ). With below-gap pumping only the intra-4f Er<sup>3+</sup> emissions were observed (see Fig. 4b). It is important to note that the Er<sup>3+</sup> PL lines exhibited slightly different fine-structures and linewidths for the two excitation wavelengths suggesting the existence of different Er<sup>3+</sup> sites in GaN. The existence of multiple Er sites in GaN prepared by SSMBE is supported by an excitation wavelength dependent study of the Er<sup>3+</sup> PL spectra. It can be noticed in fig. 5a), that

pumping resonantly into an intra-4f transition ( $\lambda_{\text{ex}} = 496.5$  nm) leads to a slightly reduced linewidth of the central 1.54  $\mu\text{m}$  emission peak (~8 nm) compared to above-gap pumping. This effect was even more pronounced for the visible emission line at ~558 nm shown in fig. 5b). Some fine structure was clearly resolved under resonant pumping with individual lines having a width ~1.4 nm. Under above-gap excitation only a broad line with a width of ~4.3 nm was observed. These results suggest that only a subset of Er<sup>3+</sup> ions are excited when pumping resonantly into an Er<sup>3+</sup> level. Moreover, it was also noticed that the visible PL lifetime was nearly single-exponential under resonant excitation compared to a non-exponential decay time observed under above-gap excitation.



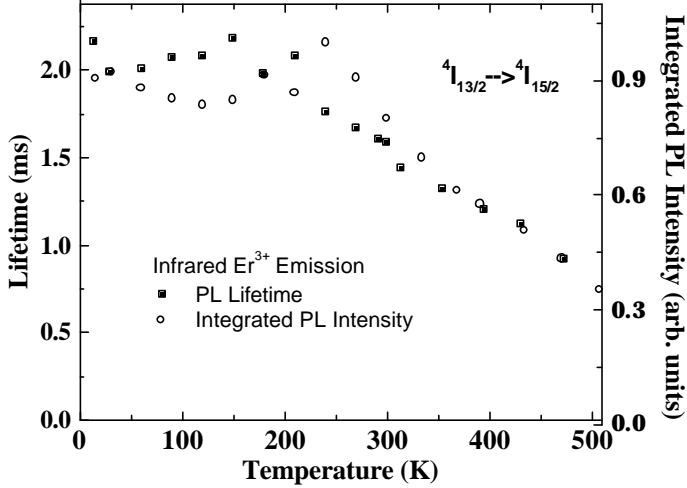
**Figure 4.** Visible and infrared photoluminescence spectra of GaN: Er (SSMBE) at room temperature (a) above-gap excitation (336–363 nm); (b) below-gap excitation (496.5 nm). Er<sup>3+</sup> transitions are indicated by their initial state. All transitions terminate in the <sup>4</sup>I<sub>15/2</sub> ground state.



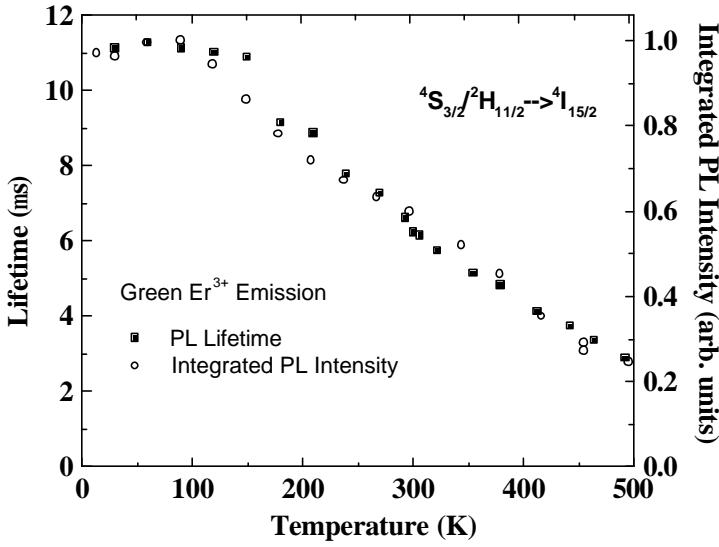
**Figure 5:** High resolution PL spectra of Er doped GaN (SSMBE) for different excitation wavelengths.

### Temperature dependent PL measurements:

In Fig. 6 the integrated  $\text{Er}^{3+}$  PL intensity and the PL lifetime for the infrared (1540 nm) line are plotted as a function of the sample temperature. The PL measurements were taken using above-gap excitation. Compared to narrow-gap semiconductors such as Si or GaAs [1], the integrated infrared PL intensity from GaN:Er was remarkably stable. Thermal quenching was less than a factor of 2 between 15 K and room temperature. At higher temperatures the integrated IR PL started to decrease and was reduced by a factor of  $\sim 3$  at 500 K relative to its low temperature value.



**Figure 6:** Comparison of the temperature dependence of the integrated PL intensity and the PL lifetime for the infrared transition of  $\text{Er}^{3+}$  in GaN ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ ).



**Figure 7.** Comparison of the temperature dependence of the integrated PL intensity and the PL lifetime for the green transitions of  $\text{Er}^{3+}$  in GaN ( ${}^4\text{S}_{3/2} / {}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ ).

A similar behavior was observed for the integrated green  $\text{Er}^{3+}$  PL intensity of the green (537 nm and 558 nm) lines, as shown in Fig. 7. With above-gap excitation, the integrated green PL intensity ( ${}^4\text{S}_{3/2} / {}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ ) remained nearly constant up to only  $\sim 150$  K, and then decreased at higher temperatures. At 500 K the integrated green PL intensity was reduced by a factor of  $\sim 3$  relative to its low temperature value. Since above-gap excitation generated a broad yellow band emission  $\sim 550$  nm, it was difficult to measure the lifetime of the

green lines. Consequently, below-gap was used and the PL lifetime was measured at 558 nm. As shown in Fig. 7, the green Er<sup>3+</sup> PL lifetimes follow the change of the associated integrated green Er<sup>3+</sup> PL intensity very closely.

In order to interpret these results, consider the temperature dependence of the PL intensity at low pump power:

$$I_{PL} \sim \mathbf{S}_{ex} \cdot \frac{w_r}{w_r + w_{nr}} = \mathbf{S}_{ex} \cdot w_r \cdot \tau \quad (3)$$

where  $\mathbf{S}_{ex}$  is the excitation cross-section,  $w_r$  is the radiative decay rate,  $w_{nr}$  is the non-radiative decay rate, and  $\tau$  is the PL lifetime ( $\tau^{-1} = w_r^{-1} + w_{nr}^{-1}$ ). As discussed earlier, the green emission lifetime is reduced with increasing temperature because of the thermalization of the <sup>4</sup>S<sub>3/2</sub> and <sup>2</sup>H<sub>11/2</sub> excited states, which are separated by only ~700 cm<sup>-1</sup>. Therefore, the <sup>2</sup>H<sub>11/2</sub> state is populated only at higher temperatures. This thermalization reduces the average green PL lifetime of ~11.2 μs at 15 K to ~6.2 μs at 300 K. At 500 K the average green PL lifetime is further reduced to less than 3 μs. The reduction in PL lifetime reflects the increase in the radiative decay rate ( $w_r$ ) at higher temperatures. Assuming that non-radiative decay processes are negligibly small for the green Er<sup>3+</sup> PL, the slight decrease of the integrated green Er<sup>3+</sup> PL intensity above ~150 K is attributed to a change in excitation efficiency. The IR Er<sup>3+</sup> PL lifetime at low temperature was measured to be ~2.1 ms and decreased to 1.6 ms at 300 K. At 500 K, the IR Er<sup>3+</sup> PL lifetime had reduced to ~0.4 ms. In contrast to the green Er<sup>3+</sup> PL lifetime, it can be assumed that the radiative decay rate of the <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition is constant. Therefore, any decrease in IR Er<sup>3+</sup> PL lifetime is attributed to the onset of nonradiative decay, which consequently decreased the integrated PL intensity at higher temperatures. The detailed mechanisms of this non-radiative decay process are still under investigation.

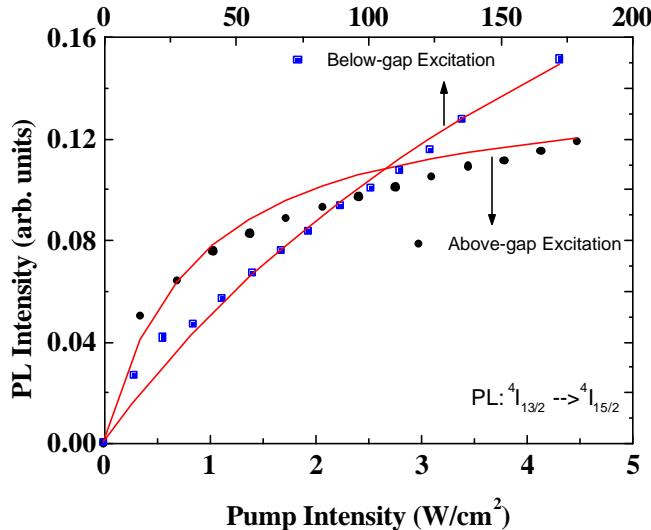
### Pump power dependent PL measurements:

To gain more insight in the excitation mechanism of Er<sup>3+</sup> ions in GaN, studies of the dependence of the PL intensity on the pump power, at different excitation wavelengths, were performed. The behavior of integrated IR Er<sup>3+</sup> PL intensity, using above-gap and below-gap excitation, is depicted in Fig. 8. With above-gap pumping (350 nm) the IR Er<sup>3+</sup> PL intensity starts to saturate at pump intensities of less than 2 W/cm<sup>2</sup>. In contrast, with below-gap excitation (514 nm) the IR Er<sup>3+</sup> PL intensity increased nearly linearly with increasing pump intensity and saturation was not observed even at pump intensities as high as 150 W/cm<sup>2</sup> (the experimental limit). It can further be noticed that the saturation levels are different for both excitation schemes. A similar pump intensity dependence was observed for the green Er<sup>3+</sup> PL for both above- and below-gap excitation.

The pump intensity dependent PL data were modeled within a simplified three level Er<sup>3+</sup> energy scheme. After balancing the rates of excitation and de-excitation under steady state pumping conditions, it can be shown that the pump intensity dependence of the IR Er<sup>3+</sup> PL is given by:

$$I_{PL} = \frac{I_{PL,max}}{\tau^{-1} \cdot h \cdot c} \cdot \frac{1}{1 + \frac{\mathbf{S}_{ex} \cdot p_{ex} \cdot I_{ex}}{I_{PL,max}}} \quad (4)$$

where  $I_{PL,max}$  is the maximum PL intensity,  $h$  is the Planck's constant,  $c$  is the speed of light,  $p_{ex}$  is the pump power, and  $I_{ex}$  is the excitation wavelength. The maximum attainable PL at high pump intensity (saturation level) is given by:  $I_{PL,max} = C \cdot N_{Er} \cdot w_r$ , where  $N_{Er}$  is the concentration of optically active Er<sup>3+</sup> ions, and  $C$  is the collection factor of the PL setup. Fitting the experimental data to eq. (4), an estimate of the excitation cross-section  $\sigma_{ex}$  can be obtained. For below-gap pumping, the fitting yielded:  $\sigma_{ex} \sim 2 \times 10^{-19} \text{ cm}^2$  and  $I_{PL,max} = 0.41$  with  $I_{ex} = 514 \text{ nm}$  and  $\tau = 1.6 \text{ ms}$  being fixed parameters.



**Figure 8.** Pump intensity dependence of the infrared PL from GaN:Er for above-gap and below-gap excitation. It is important to note the different pump intensity scales for both excitation schemes. The solid lines are the best fits to eq. (4).

This value for the below-gap excitation cross-section seems reasonable compared to the cross-sections of Er<sup>3+</sup> transitions in other hosts materials ( $\sim 10^{-20} \text{ cm}^2$ ) [10]. The slightly higher Er<sup>3+</sup> cross-section in GaN:Er could be due to defect-related Er<sup>3+</sup> excitation, which overlaps the resonant Er<sup>3+</sup> excitation. For above-gap pumping, the best-fit of the data to eq. (4) yielded:  $\sigma_{\text{ex}} \sim 1 \times 10^{-16} \text{ cm}^2$  and  $I_{\text{PL,max}} = 0.15$  with  $I_{\text{ex}} \sim 350 \text{ nm}$  and  $\tau = 1.6 \text{ ms}$  being fixed. The best-fit result indicates that the above-gap excitation cross-section is more than two orders of magnitude larger than that obtained for below-gap pumping. This value for the above-gap  $\sigma_{\text{ex}}$  is comparable to impact excitation cross-sections reported for Er-doped GaN [11] and Er-doped Si [12] in electroluminescent devices under reverse bias. These results also suggest that an efficient Er<sup>3+</sup> excitation process through carrier injection in a forward-biased light emitting diode should be possible.

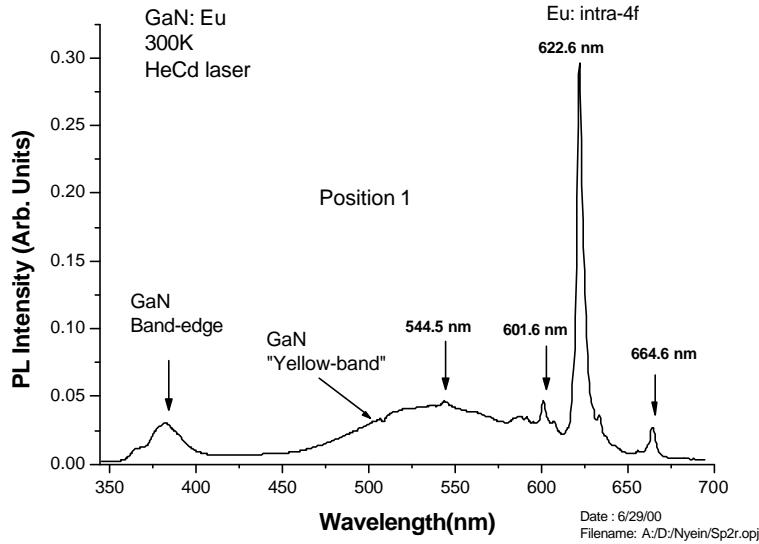
## 2. Initial Spectroscopic studies of Eu doped GaN (SSMBE)

The visible light emission from rare earth doped GaN has become of significant current interest for applications in display technology [3-4]. For obtaining red light emission, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of trivalent Eu ions seems most promising. Intense red line emission around 622 nm from Eu doped GaN has been demonstrated from several research groups [13-20] and EL devices have been fabricated [3,4,13]. The optimization of current devices requires, however, a more detailed understanding of the incorporation and emission properties of Eu<sup>3+</sup> ions in GaN.

During the last year of this project, a sample of Eu doped GaN prepared by solid-source MBE was provided by Dr. Steckl's group at the University of Cincinnati. The Eu doped GaN film was grown in a Riber MBE-32 system on 2 inch p-Si (111) substrates [13]. Solid sources were used to supply the Ga (7N purity) and Eu (3N purity) fluxes. A RF plasma source was used to generate atomic nitrogen. For the nitrogen plasma an RF power of 400 W and an N<sub>2</sub> flow rate of 1.5 sccm was used. The Ga cell temperature ranged from 870 to 890°C. A GaN buffer layer was first deposited for 10 min at a substrate temperature of 600°C. For the main growth the substrate temperature was ramped to 800°C. The Eu cell temperature was varied from 350 to 450°C for the growth of various films. The Eu concentration is estimated to be  $\sim 10^{18}$ - $10^{21}/\text{cm}^3$ .

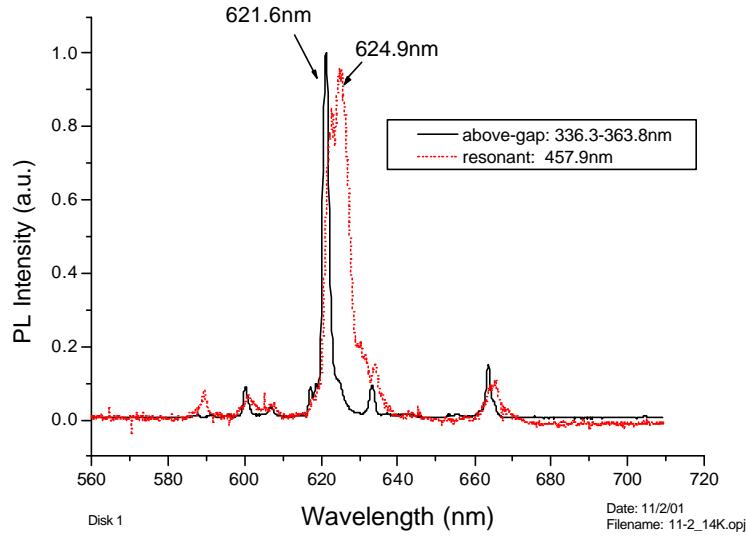
An overview of the visible photoluminescence spectrum of the investigated Eu doped GaN sample at low (15K) and room-temperature is shown in Figure 9. The emission was excited using the UV output (336-

363nm). Only weak band-edge PL from the GaN host was observed at ~365 nm. Depending on the sample position, some weak yellow-band emission was observed extending from ~450-700 nm. Superimposed on this emission were intra-4f emission lines from Eu<sup>3+</sup> ions located at ~545 nm ( $^5D_1 \rightarrow ^7F_1$ ), 601 nm ( $^5D_0 \rightarrow ^7F_1$ ), 623 nm ( $^5D_0 \rightarrow ^7F_2$ ), and 665 nm ( $^5D_0 \rightarrow ^7F_3$ ).



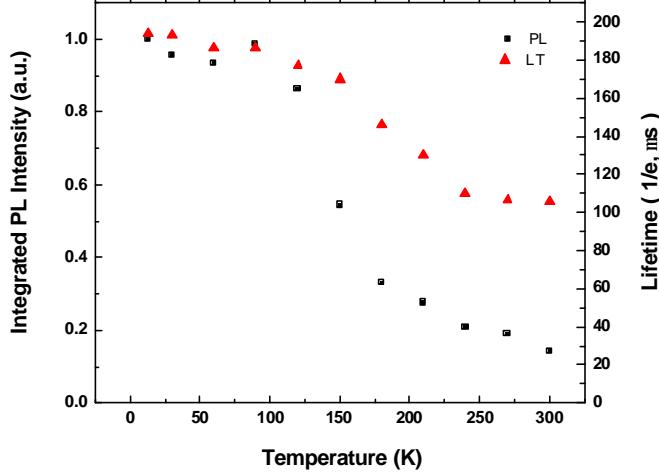
**Figure 9:** Overview of the visible emission from Eu doped GaN under above-gap excitation.

Excitation wavelength dependent emission studies were carried out on Eu doped GaN at 15K using above-gap (carrier-mediated) and below-gap (resonant) excitation. Similar to Er doped GaN, the PL spectrum of Eu doped GaN changes slightly for different excitation wavelengths. In addition, the PL lifetime changes for the two different excitation wavelengths. This observation indicates that Eu is incorporated into different sites in the GaN lattice. More site-selective PL studies are necessary to conclusively assign the lattice sites of Eu<sup>3+</sup> ions in GaN.

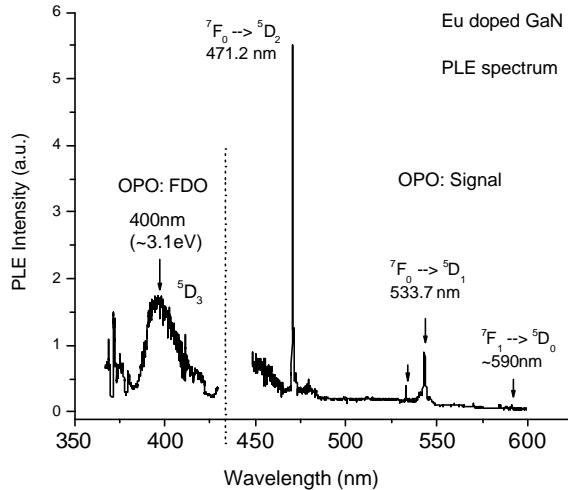


**Figure 10:** High resolution PL spectra of Eu doped GaN using above and below-gap excitation.

A temperature dependent study of the red Eu<sup>3+</sup> line showed that the integrated emission intensity decreased by more than a factor of 10 between 10 K and room temperature (figure 11). On the contrary, the emission lifetime changed only slightly (~10-20%) for the same temperature range suggesting that non-radiative decay processes are small and the Eu<sup>3+</sup> emission efficient is near unity. Therefore, the strong thermal quenching of red Eu emission is assigned to a temperature dependent pumping process. An improvement of the PL quenching behavior can be expected after the optimization of the growth parameters of Eu doped GaN.



**Figure 11:** Temperature dependence of integrated Eu PL and PL lifetime.



**Figure 12:** PL excitation spectrum of Eu doped GaN at 300K.

An initial PLE spectrum of Eu doped GaN is depicted in figure 12. Narrow intra-4f Eu<sup>3+</sup> absorption lines can be identified at ~471.2 nm ( $^7F_0 \rightarrow ^5D_2$ ); ~530-550 nm ( $^7F_0 \rightarrow ^5D_1$ ), and at ~590 nm ( $^7F_1 \rightarrow ^5D_0$ ). In addition, a broad excitation band centered at ~ 400 nm (~3.1 eV) was observed, which overlaps some higher lying Eu<sup>3+</sup> levels ( $^7F_0 \rightarrow ^5D_3$ ,  $^7F_0 \rightarrow ^5L_6$ ). Based on FTIR measurements, Bang et al. [18,19] recently reported a Eu-related defect level at 365meV below the conduction-band of GaN. A defect-related energy transfer model had been proposed in the past by several authors for the excitation of Yb<sup>3+</sup> in InP and subsequently also for Er<sup>3+</sup> for III-V's and Si [1-3]. These results suggest that for an efficient excitation of rare earth ions in GaN, an overlap of higher lying RE excited state with the RE-related defect energy is necessary in order to facilitate an efficient carrier-mediated excitation process. More comparative PLE studies of other rare earth doped GaN systems are currently in progress to further support this excitation model.

## C. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

### a) Papers published in peer-reviewed journals

J.M. Zavada, U. Hömmerich, and A. J. Steckl, "Light Emission from Rare Earth doped GaN", chapter in book entitled: "*III-V Nitride Semiconductors: Optical Properties*", Volume 13, edited by M. O. Manasreh and H. X. Jiang, Taylor & Francis Books, 2002.

J. T. Seo, U. Hömmerich, A. J. Steckl, J. M. Zavada, "Thermal quenching of Photoluminescence from Er doped GaN", Journal of Alloys and Compounds, 341, 62-66 (2002).

D. S. Lee, J. Heikenfeld, M. Garter, A. J. Steckl, U. Hömmerich, J. T. Seo, A. Braud, J. M. Zavada, "Optimum Er concentration for in-situ doped GaN visible and infrared luminescence", Applied Physics Letters, 79, 719 (2001).

U. Hömmerich, J. T. Seo, J. M. Zavada, C. Abernathy, and A. J. Steckl, "Spectroscopic studies of the visible and infrared luminescence from Er doped GaN", Materials Science & Eng. B81, 116, (2001).

J. M. Zavada, C. J. Ellis, J. Y. Lin, H. X. Jiang, J. T. Seo, U. Hömmerich, M. Thaik, R. G. Wilson, "Annealing behavior of the luminescence from erbium implanted GaN films", Materials Science and Engineering B 81, 127 (2001).

U. Hömmerich, J. T. Seo, Myo Thaik, C. R. Abernathy, J. D. MacKenzie , J. M. Zavada, "Near infrared (1.54 $\mu$ m) luminescence properties of erbium doped gallium nitride", Journal of Alloys and Compounds, 303-304, 331-335 (2000).

J. T. Seo, U. Hömmerich, J. D. MacKenzie, C. R. Abernathy, J.M. Zavada, "Near-Infrared Luminescent Device and Optical Spectroscopy of Er-doped Gallium Nitride Prepared by Metalorganic Molecular Beam Epitaxy", Journal of the Korean Physical Society, Vol. 36, 311-315 (2000).

U. Hömmerich, J. T. Seo, J. D. MacKenzie, C. R. Abernathy, A. J. Steckl, R. Birkhahn, J.M. Zavada, "Comparison of the optical properties of erbium doped gallium nitride prepared by metalorganic molecular beam epitaxy (MOMBE) and solid source molecular beam epitaxy (SSMBE)", MRS Internet J. Nitride Semicond. Res. 5S1, W11.65 (2000).

J. M. Zavada, M. Thaik, U. Hömmerich, J. D. MacKenzie, C. R. Abernathy, S. J. Pearton, R. G. Wilson, "Luminescence characteristics of Er-doped GaN semiconductor thin films", Journal of Alloys and Compounds, 300-301 (0), 207-213 (2000).

### b) Paper published in non-peer reviewed journals or in conference proceedings

U. Hommerich, J. Zavada, A. J. Steckl, "Luminescence Properties of Rare Earth doped GaN", 23<sup>rd</sup> Rare Earth Research Conference, Davis, CA, July 13-18, 2002, invited talk.

Ei Ei Nyein, U. Hommerich, J. Heikenfeld, D. S. Lee, A. Steckl, J. M. Zavada, "Spectroscopic evaluation of rare earth doped GaN for full-color display applications", Conference on Lasers and Electro-Optics/Quantum Electronics & Laser Science (CLEO/QELS) Long Beach, CA, May 19-24, 2002, Oral presentation, CFG3

J. M. Zavada, U. Hommerich, A. J. Steckl, Excitation Mechanisms of Rare Earth Ions embedded in GaN Thin Films, Electro-Chemical Society Meeting, Philadelphia, PA, May 12-17, 2002, Session: Wide Bandgap Semiconductors for Photonics and Electronic Devices and Sensors III.

Ei Ei Nyein, U. Hommerich, D. S. Lee, A. Steckl, J. M. Zavada, "Emission Properties of Er-doped GaN as a function of Ga flux, American Physical Society March 2002 Meeting, Indianapolis, Indiana, March 18-22, 2002, oral presentation, paper T18-6.

Ei Ei Nyein, U. Hommerich, Ei Ei Nyein, J. T. Seo, A. Braud, J. Heikenfeld, D. S. Lee, A. Steckl, J. M. Zavada, "Photoluminescence studies of Erbium and Europium doped GaN prepared by Solid-Source Molecular Beam Epitaxy, presented at Material Research Society Fall 2001 Meeting, Boston, MA, November 26-30, 2001.

J. M. Zavada, U. Hommerich, A. Braud, Ei Ei Nyein, J. Heikenfeld, M. Garter, D. S. Lee, R. Birkenhahn, A. J. Steckl, "Thermal Quenching Characteristics of Luminescence from RE ions in GaN Thin Film, presented at the 5<sup>th</sup> International Conference of Excited States of Transition Elements (5ESTE), Ladek Zdroj, Poland, June 6-11, 2001.

D. S. Lee, J. Heikenfeld, M. Garter, A. J. Steckl, U. Hommerich, J. T. Seo, A. Braud, J. Zavada, "Optimum Er Concentration for In-Situ doped GaN visible and IR Luminescence", presented 43<sup>rd</sup> Electronic Materials Conference, Notre Dame, IN, June 27-29, 2001, paper Z2.

Ei Ei Nyein, J. T. Seo, A. Bluiett, J. Anderson, U. Hommerich, J. Heikenfeld, M. Garter, D. S. Lee, A. J. Steckl, "Optical Spectroscopy of Europium doped Gallium Nitride prepared by Solid Source Molecular Beam Epitaxy", presented at the American Physical Society Meeting, April 28-May1, Washington, D.C., 2001, paper K20-62

C. R. Abernathy, M. Overberg, J. D. MacKenzie, U. Hommerich, S. J. Pearton, R. G. Wilson, J. M. Zavada, "Effect of impurity concentration on 1.54um emission from GaN: Er", Proc. SPIE-Int. Soc. Opt. Eng. (2000), 3942, 76-86.

U. Hömmerich, J. T. Seo, R. Birkhahn, A. J. Steckl, J. M. Zavada, "Spectroscopic Evaluation of erbium doped Gallium Nitride for Optoelectronic Applications", presented at the Opto-Southeast SPIE meeting, 18-19 Sept. 2000, Charlotte, NC, paper SE03-08.

J. M. Zavada, U. Hömmerich, J. T. Seo, A. J. Steckl, "Excitation wavelength dependent photoluminescence studies of Er doped GaN", presented at the 4<sup>th</sup> International Conference on f-elements (ICFE'4), 17-21 September 2000, Madrid, Spain, paper Co11.

U. Hömmerich, "Spectroscopic studies of the visible and infrared luminescence of Er doped GaN films", European Materials Research Society, Strasbourg, France, May 30-June 3 2000, paper 0690, invited talk.

J.M. Zavada, C. J. Ellis, J. Y. Lin, H. X. Jiang, J. T. Seo, U. Hommerich, M Thaik, R. G. Wilson, "Annealing behavior of luminescence from Erbium implanted GaN films", European Materials Research Society, Strasbourg, France, May 30-June 3 2000, paper 0342.

J. T. Seo, U. Hommerich, R. Birkhahn, A. J. Steckl, J. M. Zavada, "Optical Spectroscopy of Erbium doped Gallium Nitride prepared by Solid-Source Molecular Beam Epitaxy", 2000 March Meeting of the American Physical Society, March 20-24, Minneapolis, MN, paper V17-11.

U. Hömmerich, J. T. Seo, J. D. MacKenzie, C. R. Abernathy, A. J. Steckl, R. Birkhahn, J.M. Zavada, "Comparison of the optical properties of erbium doped gallium nitride prepared by metalorganic molecular beam epitaxy (MOMBE) and solid source molecular beam epitaxy (SSMBE)", MRS Fall 99 Meeting, Nov. 29-Dec. 3, Boston, MA, Paper W11.65.

J. T. Seo, U. Hömmerich, J. D. Mackenzie, C. R. Abernathy, S. J. Pearton, J. M. Zavada, "Near infrared (1.54 $\mu$ m) luminescent devices and optical properties of Er-doped gallium nitride", 66<sup>th</sup> Annual Southeastern Section (SES) Meeting of the American Physical Society, Nov. 7-9, 1999, Bulletin, Vol. 44, No. 6, p. 19, paper EC 1.

U.Hömmerich, J. T. Seo, Myo Thaik, C. R. Abernathy, J. D. MacKenzie, J.M. Zavada, "Er-doped III-Nitride semiconductors, novel materials for optoelectronic applications", accepted for presentation at the International Conference on Luminescence and Optical Spectroscopy of Condensed Matter, Osaka, Japan, Aug. 23-27, 1999.

U. Hömmerich, J. T. Seo, Myo Thaik, C. R. Abernathy, J. D. MacKenzie, J. M. Zavada, "Near infrared (1.54  $\mu$ m) Luminescence Properties of erbium doped gallium nitride", 22nd Rare Earth Research Conference, Argonne National Lab., July 10-15, 1999, paper PI.30.

c) Papers presented at meetings, but not published in conference proceedings

Ei Ei Nyein, J. T. Seo, U. Hommerich, "Evaluation of Eu doped GaN for phosphor applications", presented at the Virginia Academy of Science Meeting, May 23-25, 2001, Harrisonburg, VA.

d) Manuscript submitted, but not yet published

J. M. Zavada, R. G. Wilson, U. Hommerich, M. Thaik, J. T. Seo, C. J. Ellis, J. Y. Lin, H.X. Jiang, "Compositional Changes in Erbium-Implanted GaN Films due to Annealing, submitted to the Journal of Electronic Materials.

J.M. Zavada, U. Hommerich, A.J. Steckl, "Excitation Mechanisms of Rare Earth Ions Embedded in GaN Thin Films", submitted to the Journal of the Electrochemical Society.

e) Technical reports submitted to ARO

Interims report 1999

Interims report 2000

Interims report 2001

## **D. SCIENTIFIC PERSONNEL**

P.I.

Uwe Hommerich      supported 3 months during summer and 25% release time during academic year

Graduate Student:

Ei Ei Nyein:      supported since fall 2000, expected graduation date spring 2004

Undergraduate Student:

George Ofori-Boudu: supported during Summer 99, Fall 99, graduated with B.S. in Physics 2001

Osei Poku:      supported during Spring 2002

## **INVENTIONS**

none

## BIBLIOGRAPHY

- [1] G. S. Pomrenke, P.B. Klein, D. W. Langer, (Eds.), *Rare Earth Doped Semiconductors I*, Materials Research Society, Vol. 301, 1993.
- [2] S. Coffa, A. Polman, and R. N. Schwartz, (Eds.), *Rare Earth Doped Semiconductors II*, Materials Research Society, Vol. 422, 1996.
- [3] J.M. Zavada, T. Gregorkiewicz, and A. J. Steckl, (Eds.), *Rare Earth Doped Semiconductors III*, Materials Science & Engineering B, Vol. 81, 2001.
- [4] A.J. Steckl and J.M. Zavada, MRS Bulletin, 24 (9) (1999) 33.
- [5] Myo Thaik, U. Hommerich, R. N. Schwartz, R. G. Wilson, J. M. Zavada, Appl. Phys. Lett. 71 (1997) 2641.
- [6] J. T. Torvik, J. Feuerstein, J. I. Pankove, C. H. Qiu, R. and F. Namavar, Appl. Phys. Lett. 69, 2098 (1996).
- [7] J. D. MacKenzie, C. R. Abernathy, S. J. Pearton, U. Hömmerich, J. T. Seo, R. G. Wilson, and J. M. Zavada, Appl. Phys. Lett. **72**, 2710 (1998).
- [8] A.J. Steckl and R. Birkhahn, Appl. Phys. Lett. 73 (1998) 1700.
- [9] A. A. Kaminskii, “*Laser Crystals*”, 2<sup>nd</sup> edition, Springer Series in Optical Sciences, Vol. 14, Springer Verlag, New York, 1990, p.120.
- [10] S. A. Payne, L. L. Chase, L. K. Smith, W. L. Kway, and W. F. Krupke, IEEE J. Quantum Electron. 28 (1992) 2619.
- [11] J. T. Torvik, C. H. Qui, R. J. Feuerstein, J. I. Pankove, F. Namavar, J. Appl. Phys. 81 (1997) 6343.
- [12] S. Wang, A. Eckau, E. Neufeld, R. Carius, and Ch. Buchal, Appl. Phys. Lett. 71 (1997) 2824.
- [13] J. Heikenfeld, M. Garter, D.S. Lee, R. Birkhahn, and A. J. Steckl, Appl. Phys. Lett. **75**, 1189 (1999).
- [14] S. Morishima, T. Maruyama, M. Tanaka, Y. Masumoto, K. Akimoto, Phys. Stat. Sol. A **176**, 113 (1999).
- [15] H. J. Lozykowski, W. M. Jadwisienczak, J. Han, I.G. Brown, Appl. Phys. Lett. **77**, 767 (2000).
- [16] T. Monteiro, C. Boemare, M. J. Soares, R. A. Sa Ferreira, L. D. Carlos, K. Lorenz, R. Vianden, E. Alves, Physica B **308-310**, 22 (2001).
- [17] M. Overberg, K.N. Lee, C. R. Abernathy, S. J. Pearton, W. S. Hobson, R. G. Wilson, J. M. Zavada, Materials Science and Engineering **B81** 150 (2001).
- [18] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, and E. Yagi, Phys. Stat. Sol. (b) **228**, 319 (2001).
- [19] H. Bang, S. Morishima, Z. Li, K. Akimoto, M. Nomura, E. Yagi, J. Crystal Growth **237-239**, 1027 (2002).
- [20] Z. Li, H. Bang, G. Piao, J. Sawahata, K. Akimoto, J. Crystal Growth **240**, 382 (2002). Appl. Phys. Lett. **71**, 2662 (1997).